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Issued March 9, 1907.

U. S. DEPARTMENT OF AGRICULTURE,
FOREST SERVICE—Circular 80.
GIFFORD PINCHOT, Forester.

THE FRACTIONAL DISTILLATION OF COAL-TAR CREOSOTE.

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THE FRACTIONAL DISTILLATION OF COAL-TAR CREOSOTE.

Timber preservation is playing an increasingly important rôle in the conservation of our National forest resources, and on this account the preservation experiments conducted by the Forest Service are becoming a more and more important part of the work of the Service. In keeping accurate records of this experimental work, it is extremely desirable to have the best possible analyses of the various creosotes used.

In Bulletin No. 72 of the American Railway Engineering and Maintenance of Way Association there is a voluminous discussion of the best way of analyzing creosote. This discussion brought out the fact that there is a wealth of divergent opinions on this subject, but a rather meager available supply of experimental data. This divergence of opinion indicates the great need of reliable information on the influence of the various effective factors in the fractional distillation of creosotes. Although it may be desirable that an analysis as empirical as that of creosote should be carried out in the same way by all analysts, the Forest Service believes it to be a mistake to adopt for its own use any method except that which is known to give the best results consistent with a reasonable simplicity.

We assume that everyone interested in creosote analysis is familiar with the method proposed last year by Von Schrenk, Fulks, and Kammerer, which was taken, with slight alterations, from the method long used by the American Telephone and Telegraph Company. In the early part of 1906 a report was made to the Forest Service by Dr. Gellert Alleman of work which he had been doing on the analysis of creosote oils extracted from timbers which had seen long service. In this report Doctor Alleman described the method of analysis which he employed, and gave some of the reasons which led him to this method. A statement of this method and the reasons for it are given below in Doctor Alleman's own words. It is evident at once that this method is quite different from that in use by the American Telephone and Telegraph Company and by those who follow the procedure recommended by Doctor von Schrenk and his coworkers.

> In England, and to some extent in Germany and the United States, the vessel specified as the distilling vessel is the usual glass retort with a tubulus through which the thermometer is inserted. The great objection to a retort is that on account of variation in size, shape, and especially of the size of the neck, uniform results are extremely difficult to obtain.
>
> The position of the bulb of the thermometer, relative to the outlet tube, is the most important cause of variation in distillations made from different retorts, and at

the high temperatures used in distilling these samples, the size of the outlet also plays a most important part in producing variations in results obtained under the influence of approximately the same conditions of heat. Usually an 8-ounce (240 c.c.) retort is specified. "An 8-ounce retort" is a most indefinite description and interpreted variously by different dealers. Usually it is understood to mean that the bulb part of the retort, when the latter is placed at the proper angle for distillation, is to hold 8 ounces. The use of a retort was suggested by the tar distillers because it was used by them to make rough tests at the works.

The proposition can be stated without fear of successful contradiction that whenever accurate and scientific tests can be applied to commercial articles, and these tests do not involve any great cost or elaborate apparatus, they should replace the older and more crude commercial tests first employed.

In practically all scientific laboratories, where accuracy is required in the distillation of small amounts of volatile materials, retorts are now disregarded on account of the variations obtained by their use, and various forms of distilling bulbs are employed. These bulbs are made with the outlet tube respectively near the top, about the middle, and low down on the neck of the bulb; the one best adapted to creosote fractionation has the outlet somewhat below the middle of the neck. The delivery tube should be 40 cm. long, otherwise there is danger of igniting the first distillates by the flame used in distilling.

In order to record the temperature of the oil passing over as vapor, the thermometer should be placed with the mercury bulb just below the outlet tube.

An important variation in the results is dependent upon the mode of application and amount of heat. If the distillation is hurried so that approximately more than 3 drops per second pass over, the temperature indicated by the thermometer will be too high.

A Bunsen burner is the usual source of heat, and the distilling bulb is placed on a thick piece ($\frac{1}{2}$ inch) of asbestos board, through which a hole about $1\frac{1}{2}$ inches in diameter has been cut. The board can be supported on an iron tripod, or, more conveniently, on a ring stand. The advantage of such a board, so cut, is that practically all radiation of heat from the lamp to the thermometer is cut off. When the bulb is supported by a clamp without any outside protection, or when it is placed on a wire gauze, the temperature of the thermometer is influenced by radiation. The writer has experimented considerably with various forms of burners, and is inclined to the belief that a number of very small flames, such as can be obtained by making a Tekla attachment to a Bunsen burner, or by using a very small ring burner, or preferably a Rogers burner, in which latter the flames form radii and extend toward the center, and which are under minute control by means of a screw regulating the supply of gas, are to be preferred as giving a more uniform and quiet distillation. No matter what form of burner is used, an accurate gas regulator should be introduced between the burner and the supply of gas, so that the flame can be regulated to the most minute detail. The indicators admit of obtaining a flame of a certain intensity at a given time, and with a little experience in distilling oils the flame can be so increased every two or three minutes by means of these regulators that uniform distillations can be obtained.

Many of the specifications first published in England state that the distillation of the sample is to be carried out under conditions similar to those employed in the distillation of crude coal tar on a large scale; namely, the immersion of the bulb of the thermometer in the oil during the distillation and taking account of the amount of the fractions as follows:

To 170° C.
170° C. to 230° C.
230° C. to 270° C.
270° C. to 400° C.

These tests are still adhered to in England. In other words, it was assumed that by this procedure the relative amounts of light oil, carbolic oil, creosote oil, and anthracene oil would, respectively, separate.

This assumption is not in accordance with the facts, as might be expected, for the reason that the creosote oil is an entirely different mixture from the original crude coal tar, and consequently the temperatures at which these various compounds or mixtures volatilize are materially altered.

When a complex mixture, such as creosote, is distilled, the various distillates passing over do not volatilize at the exact boiling points of the individual compounds which they contain, and the compounds can not be separated in the pure state except by repeated distillations. If all creosote oils were similarly constituted, then by by means of a series of analyses it could readily be determined at what temperatures the various constituents volatilize; but since oils vary greatly in composition, this is not possible, and whatever temperatures are determined upon for the separation of the various fractions, these temperatures are in a measure arbitrary. For instance, if an oil is rich in naphthalene, and also contains a certain amount of material distilling below 200° C., some of the naphthalene is liable to volatilize with or be carried over mechanically by the lighter oil, and the naphthalene will all be volatilized when a temperature of 245° C. is reached. On the other hand, if the oil contains a large amount of the higher boiling constituents, such as anthracene, and also a considerable amount of naphthalene, the latter is frequently not gotten rid of before a temperature of 250° C. is reached. The point at which naphthalene ceases to come off, if it is present, can be determined by allowing a drop of the distillate supposed to contain naphthalene to fall on a piece of cold porcelain; if it solidifies the presence of naphthalene is indicated.

In over 800 distillations conducted by the writer it was found that 92 per cent of those oils which contained naphthalene gave the latter off between 205° C. and 245° C., and one of the fractions has consequently been taken between the temperatures indicated.

After conducting tests on a great many oils, the writer is of the opinion that the most information can be obtained by taking recognition of the distillates as follows:

1. To 170° C.
2. 170° C. to 205° C.
3. 205° C. to 245° C.
4. 245° C. to 270° C.
5. 270° C. to 320° C.
6. 320° C. to 420° C.
7. Residue above 420° C.

Fraction No. 1 contains the light oil and water. In case much water is present, some of the naphthalene will frequently volatilize with it; No. 2 should contain phenol and the cresols; No. 3 should contain naphthalene and the two methyl-naphthalenes; the naphthalene and the two methyl-naphthalenes crystallize out and can be removed by filtration, and the solid naphthalene determined. No. 4 contains, among other compounds, dimethyl-naphthalenes; No. 5 is usually entirely liquid on cooling, and its composition is complex and variable. In case little anthracene oil is present, some of it will be found in this distillate. No. 6 usually contains anthracene oil, phenanthrene, acridine, etc., and, on cooling, solidifies. The residue above 420° C. may contain practically the same as No. 6 and also tar.

The amount of oil distilled should be at least 200 grams.

The important differences between the method proposed by Doctor Alleman and the methods of the American Telephone and Telegraph Company and Doctor von Schrenk are chiefly in the nature of the apparatus used, and in the temperatures between which fractions are taken. Experimental work has, therefore, been undertaken to obtain data on the influence which the character of the distilling vessel has upon the results of the fractional distillation of creosote. This involved (1) a determination of the differences in the percentage weights distilling between the same temperatures when using a side-necked flask and a retort, (2) the differences in the composition of the fractions distilling between the same points when using the flask or the retort, and (3) a study of the differences in the percentage weights of the fractions due to the size of the distilling vessel. Some data have been obtained on the influence exerted by the rate at which a distillation is conducted, and a study was also made to show the temperatures between which fractions should be taken, in order to give the greatest information concerning the composition of the creosote under examination.

It should be understood at the outset that the results given here are not wholly complete, and that no attempt is made at this time to define the method to be employed in the Forest Service analyses. It is deemed desirable, however, to get these experimental results before the users of creosote in order that the benefit of their criticisms and suggestions may be had.

Thanks are due to Dr. H. W. Jayne, of the Barrett Manufacturing Company, for his helpful cooperation in obtaining samples of creosote of widely different composition.

THE INFLUENCE OF THE VESSEL ON THE FRACTIONAL DISTILLATION OF CREOSOTE.

Numerous experiments have been conducted to discover the fundamental laws which underlie the separation of liquids by means of fractional distillation. In doing this work investigators have found it necessary to work, for the most part, with simple mixtures—that is, mixtures of two or three substances; but the principles worked out with simple mixtures have been found to be applicable to complex ones in the cases in which these have been carefully studied.

It is a well-known fact that when a mixture of substances is distilled the individual component substances do not vaporize at the same boiling points as when pure, and that therefore the vapor at any temperature during distillation is composed of a mixture of the constituents in the still. A fractional distillation is successful in just so far as the vapors of those substances which have volatilized below their boiling points are condensed and returned to the still, and maximum quantities of the vapors of the constituent substances pass over into the condenser at approximately their boiling points when in the pure state. To get a good fractionation it is therefore necessary that there should be some condensation and reflowing, and the more completely the ascending vapor is washed by the condensed liquid which is flowing back into the still the better is the resulting separation. To bring about this washing of the vapors by the condensed liquid various forms of apparatus have been devised, some of which are very effective.

The successful application of the general principles of fractional distillation to the specific problem of creosote analysis is rendered extremely difficult by the extraordinary complexity and variability of this product. It is wholly impossible to calculate the results to be obtained in any fractionation, both because of the large number of the compounds present and the fact that the properties of many of them are practically unknown. The problem is further complicated by the great range of temperature through which the distillation must be continued.

A specific objection to the employment of any efficient fractionating device has been brought out in the discussion which was printed in Bulletin No. 72 of the American Railway Engineering and Maintenance of Way Association. In a footnote to page 46 the chemist of the firm of Burt, Boulton & Haywood makes the assertion that the fractional distillation of creosote is accompanied by a decomposition of the oil, and points by way of proof to the presence of a pitchy residue after distillation, the constituents of which, he states, do not exist in the oil before distillation. If such decomposition does in fact take place this will so greatly complicate the problem of creosote analysis that it will be necessary to waive all other considerations and conduct the distillation so as to reduce decomposition to a minimum.

When one remembers the way in which the components of coal tar are formed and the nature of the compounds themselves, it seems rather improbable that the relatively moderate heat required for fractional distillation should cause any decomposition worthy of note, and the difficulty of "cracking" the aromatic hydrocarbons composing creosote is well known to gas makers. Moreover, it is to be expected that during the distillation of creosote from crude tar a small amount of certain substances should pass over at temperatures far below their true boiling points, so that at the end of an ordinary creosote analysis there should be a certain quantity of these very high boiling substances remaining behind and forming a pitchy residue.

If it is true that this residue is composed of substances resulting from decomposition during the fractional distillation of the creosote, then if after fractionation the fractions are poured back into the vessel from which they have just been distilled and the whole distilled once more, the residue should be greater after the second fractionation than after the first, since it should now consist of the pitch formed in the first distillation, plus the pitch formed in the second. The experiment of returning the fractions to the distilling vessel and redistilling has been tried with a number of creosotes, and the results are given in Table 1.

Table 1.—*Influence of redistillation on the percentage of residue.*

Creosote No.	Distilling vessel.	Weight of oil distilled.	Distillation stopped at—	Weight of residue.	
				First distillation.	Second distillation.
		Grams.	°*C.*	*Per cent.*	*Per cent.*
9	250 c. c. retort	100	315	17.06	18.07
10	.....do	100	315	12.05	11.00
3	500 c. c. flask	250	320	24.40	24.80
5	.....do	250	320	15.21	14.00
10	.....do	250	320	7.22	7.20
	Average			15.19	15.01

The results of these five experiments are sufficient to show that the residue remaining in the distilling vessel is not altered by repeating the distillation, since the variations shown are all within the limit of experimental error.

It is frequently noticed, at the end of the distillation, when the heat is shut off and air is sucked back into the condenser and still, that the drops of distillate present in these places undergo a rapid darkening. This would seem to indicate that the darkening which is observed in creosotes may be due, in part at least, to oxidation. The influence of oxygen was further shown by dividing the light-yellow liquid distillate obtained from a creosote between 250° and 280° into two portions, one of which was placed in an atmosphere from which the oxygen was taken up by a pyrogallol and sodium hydroxide mixture and the other kept in ordinary air. On comparing the color of the two oils after three days' standing, it was seen that the one kept in the presence of oxygen had darkened to much the greater extent.

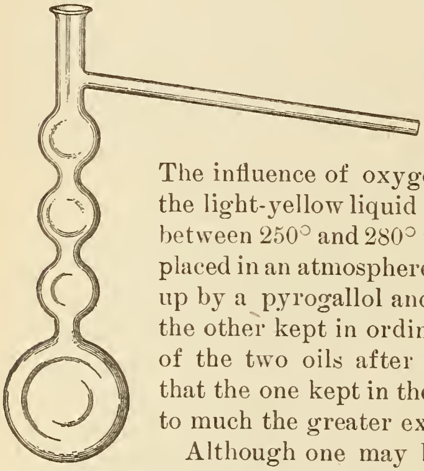

Fig. 1.—Three-bulb Ladenburg flask.

Although one may be decidedly skeptical concerning the decomposition of creosote during its fractionation, the fact that the last part of the distillation of many oils must be conducted at a high temperature makes it impossible to use some of the complicated still heads which have proved so efficient with low-boiling mixtures. The experiments so far have been directed to testing the comparative efficiency of the retort and the ordinary side-neck distilling flask, and to carrying out a few experiments with the three-bulb Ladenburg fractioning flask.

WEIGHT OF FRACTIONS OBTAINED WITH FLASK AND RETORT.

Table 2 shows the percentage weights of the fractions distilling from the same creosotes in different distilling vessels. These were, respectively, the 250 c. c. retort, the 200 c. c. side-neck flask, and the 3-bulb Ladenburg flask.

TABLE 2.—*Influence of the distilling vessel on the weight of fractions.*

CREOSOTE NO. 13.

Temperature (degrees centigrade).	Percentages by weight of fractions.		
	250 c. c. retort, 100 gms. oil (average of 2 distillations).	200 c. c. bulb, 100 gms. oil (average of 2 distillations).	500 c. c. 3-bulb Ladenburg flask, 200 gms. oil.
170–205	0.30	1.52	1.12
205–245	28.95	29.33	29.64
245–270	17.03	14.75	14.23
270–320	19.79	19.91	19.34
320–360	22.45	21.15	35.41
Residue	11.13	13.19	
Total	99.65	99.85	99.74

CREOSOTE NO. 46.

Temperature (degrees centigrade).	Percentages by weight of fractions.		
	250 c. c. retort, 100 gms. oil.	200 c. c. bulb, 100 gms. oil.	500 c. c. Ladenburg flask, 200 gms. oil.
200	....	1.04	1.78
200–210	6.30	10.24	10.05
210–235	58.50	53.69	51.15
235–270	14.48	16.42	17.48
270–315	10.43	9.56	10.18
Residue	9.89	8.64	9.06
Total	99.60	99.59	99.70

CREOSOTE NO. 14.

Temperature (degrees centigrade).	Percentages by weight of fractions.		
	250 c. c. retort, 100 gms. oil (2 distillations).	200 c. c. bulb, 100 gms. oil.	500 c. c. Ladenburg flask, 200 gms. oil.
170	1.67	2.26	3.29
170–205	10.49	12.76	11.87
205–245	45.74	42.10	43.77
245–270	12.85	14.03	12.67
270–320	17.31	16.82	16.42
Residue	11.48	11.65	11.61
Total	99.54	99.62	99.63

CREOSOTE NO. 39.

Temperature (degrees centigrade).	Percentages by weight of fractions.		
	250 c. c. retort, 100 gms. oil (2 distillations).	200 c. c. bulb, 100 gms. oil (2 distillations).	500 c. c. Ladenburg flask 200 gms. oil.
170	0.67	0.87	1.84
170–205	15.09	17.95	17.22
205–245	53.38	49.92	49.89
245–270	9.42	9.50	9.40
270–320	11.11	11.18	11.22
Residue	9.79	10.09	10.19
Total	99.46	99.51	99.76

In carrying out these experiments every precaution was used to prevent variations arising from any other cause than the character of the distilling vessel. The thermometers used had been tested at the Bureau of Standards, and were, therefore, of known accuracy. All of the samples from any one creosote were weighed at the same time and kept tightly stoppered until analyzed, thus preventing any subliming of the naphthalene and consequent alteration of composition. In using the retort the apparatus was set up in accordance with the recommendations in the paper by Von Schrenk, Fulks, and Kammerer, except that the source of heat, as in the case of flask distillations, was an Erlenmeyer-Argand burner, a form of burner which has been found to be particularly well adapted for this work. In using the flask for distillation a piece of asbestos board with a hole about 2 inches in diameter was used, instead of wire gauze, and no asbestos cover was placed around the still. The same condensing tube used for retort distillations was employed for flask distillations.

In the case of creosote No. 13 a detailed fractionation was conducted, both with the Ladenburg flask and with the ordinary side-neck flask. With the Ladenburg flask, 14 fractions were taken up to a temperature of 320° C.; with the ordinary flask, 15 fractions were taken up to a temperature of 385°. The results are plotted in the form of the curve shown in figure 2.

It will be seen from the tables and curves that the percentages of a creosote oil which distilled between certain temperatures underwent but slight variation when the character of the distilling vessel was altered.

THE COMPOSITION OF THE FRACTIONS OBTAINED WITH FLASK AND RETORT.

The fact, however, that the character of the distilling vessel has but slight influence on the weight of the oil distilled between certain temperatures does not prevent a wide difference in the composition of the fractions having the same weight. For example, the naphthalene fraction might weigh the same when distilled from a flask as when distilled from a retort, yet the amount of naphthalene actually present in the two fractions be quite different, and it would follow that in the case where the naphthalene came over in the narrower temperature range a better separation had been effected. In order to obtain some data on this point, comparative estimations have been made of the solids present in the distillates obtained from the same creosote between the same temperatures when using the flask and the retort. The solids obtained from the lower boiling fractions are composed, for the most part, of naphthalene, whereas the solids separating from the high boiling fractions consist of the various solid constituents of anthracene oil.

It required considerable experimentation to devise a method for estimating naphthalene which would give comparable results. The method settled upon, which consists of freezing out the naphthalene and pressing out the residual oil, is as follows:

Two freezing mixtures are prepared by using for each 150 grams of ice, 100 c. c. of water, and 10 c. c. of concentrated sulphuric acid.

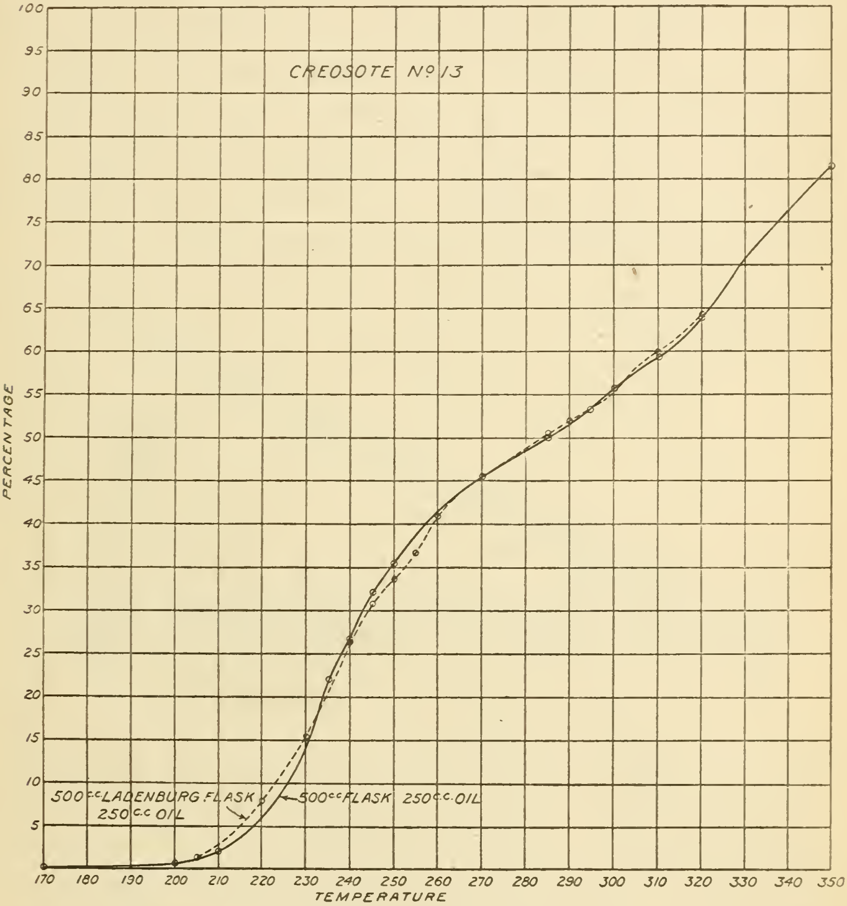

FIG. 2.—Comparative distillations from ordinary distilling flask and from 3-bulb Ladenburg flask.

A straight-sided metal cup, with finely perforated bottom, provided with an iron plunger which just fits it, is used for filtering the naphthalene. A filter paper of a slightly larger diameter than that of this perforated cup is fitted in the bottom with the aid of the plunger. The cup with the filter paper, the plunger, and two more filters for covering the naphthalene are placed in a beaker in one of the freezing mixtures.

The oil in which naphthalene is to be estimated is melted and a sample not exceeding 10 c. c. placed in a small beaker. The beaker is set in the other freezing mixture and the oil stirred with a spatula until crystallization is complete. The beaker and freezing mixture are then covered with a watch crystal and allowed to stand for ten minutes. Just before the end of the ten-minute period, the cup with the paper in its bottom, together with the two similar papers for covering, is weighed. The naphthalene in the beaker is stirred once more, and as much as can be conveniently removed with the spatula is placed in the metal cup and another weight taken as quickly as possible. The two extra filter papers are placed on top of the naphthalene and carefully adjusted with the iron plunger. The crucible containing the frozen oil and the plunger are placed again in the freezing mixture, covered with a watch glass, and kept there for ten minutes to make sure that the whole is at 0° when the oil is pressed out.

After this second cooling, the crucible is placed on a folded wire gauze and a pressure of 50 pounds exerted on top of the plunger for two minutes. After two minutes of the 50 pounds pressure, the weight is increased to 100 pounds for two minutes. The cup is then removed, a pad of blotting paper substituted for the wire gauze, the plunger taken out, and the several small disks of blotting paper placed on top of the filter papers which lie over the naphthalene, the plunger replaced, and a pressure of 100 pounds exerted for five minutes. After this period the blotting papers are changed for fresh ones, and 100 pounds pressure is exerted for another five minutes. The blotters are then changed, and a third and fourth five-minute period of pressure employed. At the end of this time the blotting papers and plunger are removed, and the cup, after being wiped clean, is weighed again. In cases where there is a large percentage of naphthalene, yet another five minutes of pressure should be given after the weighing to make sure that no significant quantity of oil can be expressed by such a treatment. The apparatus used in exerting pressure is shown in figure 3.

Although duplicate estimations usually agree within one-half of 1 per cent, and the method is good for comparative work, this method offers opportunity for several errors in estimating the absolute quantity of naphthalene. At the end of the freezing period the naphthalene in the beaker is at a temperature of very nearly 0° C. The freezing mixture surrounding the beaker stands between $-2°$ and $-3°$. As shown by the following experiment, all of the naphthalene present does not separate at that temperature.

A quantity of the distillate obtained from creosote No. 14 between temperatures of 205° and 215° C. was placed for ten minutes in the usual freezing mixture. The frozen mass was placed on absorbent cotton laid in the bottom of a perforated cup. Suction was applied to the bottom of the cup and the top of the mass was pressed with a chilled pestle. In this way about 10 c. c. of perfectly clear oil was expressed from the crystalline mass. This oil, which might or might not contain naphthalene, was placed in a freezing mixture of hydrochloric acid and snow at a temperature of −11°. After ten minutes a small quantity of what appeared to be naphthalene crystals had separated in this oil. Seven cubic centimeters of this material were then quickly poured into a graduated centrifugal tube and whirled at a very high rate of speed for one and one-fourth minutes. This separated the material into a layer at the bottom containing a large amount of a white solid, and a clear yellow oil above. The supernatant oil was removed with a pipette, leaving 2.2 c.c. of mixed oil and crystals. This mixture was placed again in the freezing mixture at −11° and kept there for ten minutes. At the end of this time a determination of naphthalene was made according to the regular method, except that the weather conditions rendered it possible to carry out the whole test at a temperature of −11° C. The result of this experiment showed that when the oil pressed from the naphthalene at 0° was lowered to −11°, 8.7 per cent of solids separated from it. The solids expressed at −11° had a melting point varying between 71.5° and 74.5°. Some of this solid was recrystallized from alcohol, and it then melted at 79.5° to 80°. The melting point of naphthalene is variously given at 79° and 80°. Solids which had been expressed at 0° from the distillate obtained at 205° to 210° from creosote No. 14 melted at 73° to 76°. When these solids were recrystallized from alcohol the melting point was 79.5° to 80°. The results of this experiment show that in the case of the lower boiling fractions, the solid which is obtained by the repeated pressings with 100 pounds of pressure is nearly pure naphthalene and when the oil expressed at this temperature is cooled to −11°

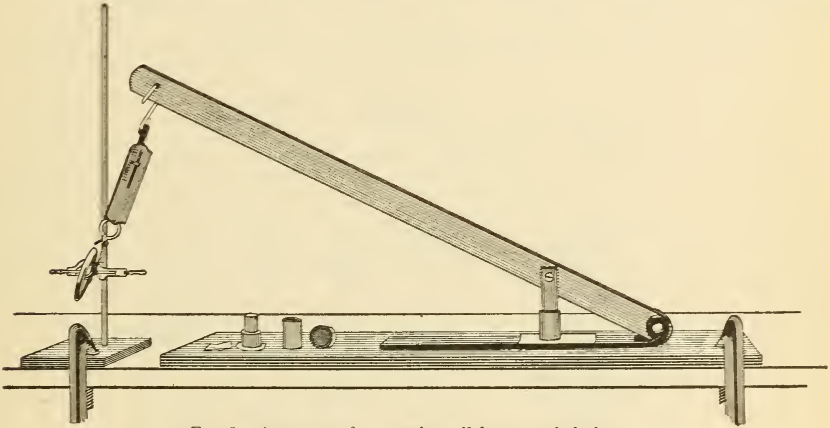

Fig. 3.—Apparatus for pressing oil from naphthalene.

a further small amount of naphthalene separates. This error would tend to make the naphthalene estimations come too low. On the other hand, the pressed naphthalene still holds a small amount of oil, and the filter papers which were weighed dry at the beginning of the determination are saturated with oil in the final weighing. These two facts would tend to make the naphthalene determinations run too high. The two errors tend to neutralize one another, and it may therefore be concluded that this method of estimating naphthalene gives results which are fairly close to the actual content. No attempt has been made to determine the composition of the solid product which is obtained from the high boiling fractions, but it probably consists of a mixture of a considerable number of substances, among which are anthracene, phenanthrene, chrysene, etc.

Four different creosotes of quite different characters were distilled from retort and flask, and the naphthalene and solid anthracene oil estimated in each fraction. The results are given in Table 3.

TABLE 3.—*The influence of the distilling vessel on the composition of the fractions.*

Temperature (degrees centigrade).	Percentage of solids at 0° in fractions.		Grams of solids at 0° in fractions.	
	250 c. c. retort.	200 c. c. flask.	250 c. c. retort.	200 c. c. flask.
Creosote No. 13:				
205–245	47.5	47.2	13.29	13.9
245–270	35.8	41.1	6.14	6.0
270–320	22.8	23.8	4.63	4.63
320–360	60.1	67.4	13.61	14.47
Creosote No. 14:				
170–205	16.4	12.0	1.70	1.56
205–245	38.0	46.9	17.54	18.33
245–270	22.1	23.3	2.80	4.08
270–320	18.6	17.9	3.18	2.89
Creosote No. 39:				
170–205	16.2	15.2	2.22	2.50
205–245	34.8	38.8	19.04	19.94
245–270	11.1	9.8	1.09	.97
270–320	15.9	(*a*)	1.71	....
Creosote No. 46:				
200–210	48.2	44.9	3.04	4.60
210–235	58.5	58.2	34.22	31.25
235–270	27.5	22.3	3.98	3.66
270–315	19.1	20.7	1.99	1.98

a Analysis lost.

The attempt has been made to express the results of these analyses graphically by plotting the grams of solids against grams of distillate. The curve is cumulative, and any point is intended to show by the vertical distance the total grams of solids which have distilled up to that point, and by the horizontal distance the total grams of distillate at that point. If a pure substance which was solid at 0° C. were distilled, every point on the curve would have equal horizontal and vertical values, and the curve would be a straight line rising at an angle of 45°. If a pure liquid substance were being distilled, the curve would coincide with the base line. If a creosote were perfectly fractioned so that the solid and liquid constituents came over in an unmixed condition,[a] the curve would consist of alternate horizontal straight lines, and straight lines rising at 45°. If no fractionation were accomplished, the curve would be one straight line rising uniformly throughout, signifying that the solids and liquids were coming over in the same proportions at every point in the distillation. The

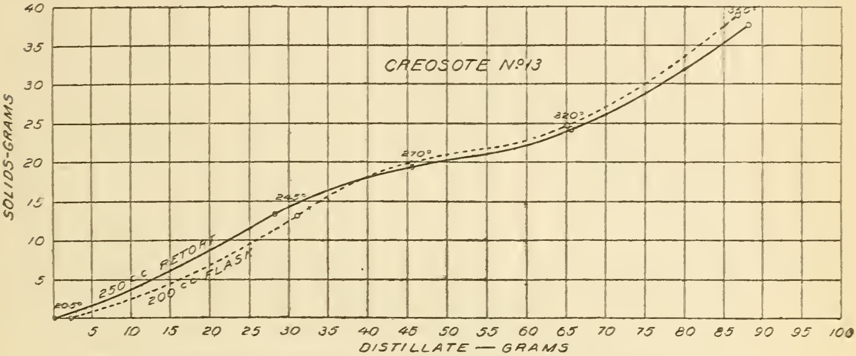

FIG. 4.—Distribution of solids in flask and retort distillations of creosote No. 13.

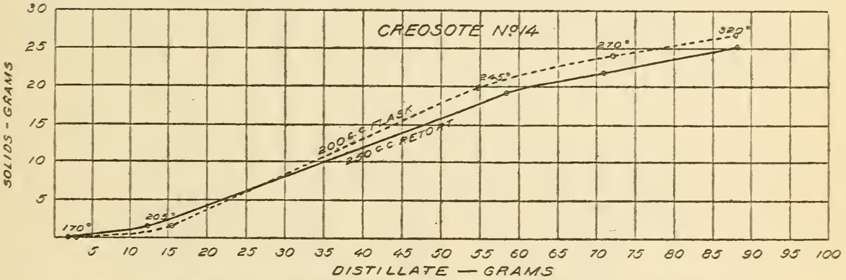

FIG. 5.—Distribution of solids in flask and retort distillations of creosote No. 14.

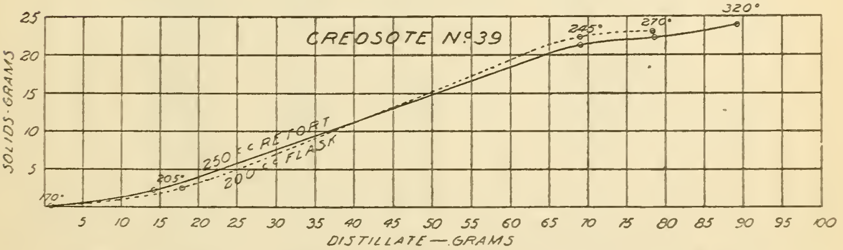

FIG. 6.—Distribution of solids in flask and retort distillations of creosote No. 39.

better fractionation in any case is therefore shown by the curve which most nearly approximates to alternate horizontal and 45-degree straight lines. The curves are given in figures 4 to 7.

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[a] This is based on the assumption that there are not liquid and solid substances in creosote boiling at the same temperatures, an assumption which may not be in accord with the facts.

It will be seen from these results that with creosotes 13, 14, and 39 a somewhat better separation was effected with the flask; with No. 46 the difference is scarcely appreciable.

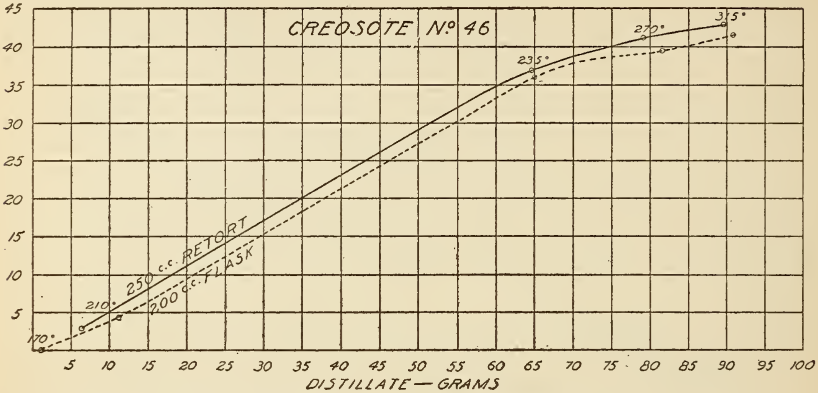

FIG. 7.—Distribution of solids in flask and retort distillations of creosote No. 46.

THE INFLUENCE OF THE SIZE OF THE DISTILLING VESSEL.

As long as the relation between the amount of creosote used and the size of the distilling flask is the same, the weights distilling between certain temperatures are practically constant for the same oil. This fact is brought out by the results tabulated below.[a]

TABLE 4.—*Influence of the size of the distilling flask.*

Temperature (degrees centigrade).	200 c. c. flask, 100 gms. oil.	500 c. c. flask, 250 gms. oil.	500 c. c. flask, 100 gms. oil.
Creosote No. 13:	*Per cent.*	*Per cent.*	*Per cent.*
170	0.19	0.31	0.18
170–205	1.70	2.41	2.80
205–245	32.17	32.53	34.01
245–270	13.35	13.20	10.98
270–320	20.22	20.76	22.09
320–360	21.25	19.76	20.27
Residue	10.29	10.76	9.03
Total	99.17	99.73	99.33
Creosote No. 14:			
170	3.18	2.59	4.19
170–205	12.11	11.52	11.45
205–245	44.91	45.49	44.86
245–270	12.88	13.08	12.51
270–320	15.27	16.23	14.94
320–350	7.12	7.08	6.89
Residue	4.01	3.77	4.85
Total	99.48	99.76	99.69
Creosote No. 15:			
170	1.33	1.08	2.31
170–205	12.41	12.77	14.76
205–245	58.22	59.53	56.34
245–270	9.67	8.58	9.09
270–320	10.47	10.72	10.27
320–350	....	....	....
Residue	7.76	7.15	7.17
Total	99.86	99.83	99.94

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[a] These are the only distillations recorded in this paper which were made with an unstandardized thermometer. The same thermometer was used throughout, so that the results are comparable, although subsequent distillations with corrected instruments showed that the absolute values are not quite right.

THE INFLUENCE OF THE RATE OF CREOSOTE DISTILLATIONS.

As a general rule, fractional distillations should be carried out slowly. A distillation running so that the distillate falls at the rate of 1 drop per second, or, better still, 1 drop in two seconds, will usually give better results than one which is carried along at a faster rate. The reason for this is obvious, since the slower distillation allows a better condensation and washing of the vapors. Comparative distillations with both flask and retort have been conducted on three different creosotes to determine what influence variations in the rate of distillation may have on the weights of the fractions obtained. The distillations were run at the rate of 1 drop per second, 2 drops per second, and between 3 and 4 drops per second. In order to regulate the speed as nearly as possible at these rates, we have made use of a metronome of the ordinary form used in musical work. The instrument was set at the desired speed, and the attempt made to have the drops of distillate fall with the ticks of the instrument. The results obtained from these comparative distillations are given in Table 5.

TABLE 5.—*Influence of the rate of distillation.*

Temperature (degrees centigrade.)	250 c. c. retort, 100 grams oil.			200 c. c. flask, 100 grams oil.		
	1 drop per second.	2 drops per second.	3–4 drops per second.	1 drop per second.	2 drops per second.	3–4 drops per second.
Creosote No. 40:	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
205	6.63	9.27	6.94	7.39	6.48	8.27
205–245	56.88	55.27	58.89	54.93	58.51	57.29
245–270	10.50	10.68	11.22	10.76	10.66	10.77
270–320	13.32	14.35	13.08	14.30	13.59	14.56
Residue	12.39	9.76	9.18	11.37	10.34	9.27
Creosote No. 43:						
170–205	....	....	....	....	.23	.02
205–245	16.96	15.81	14.69	15.26	12.59	13.70
245–270	17.55	20.17	18.06	17.96	42.51	20.11
270–320	24.23	22.25	25.11	22.17	....	22.96
320–360	28.01	28.65	28.65	28.39	28.58	27.73
Residue	12.72	12.60	12.93	15.90	15.69	14.78
Creosote No. 44:						
170	....	....	....	.35	.43	.48
170–205	9.63	6.52	11.43	8.09	8.61	10.37
205–245	49.15	53.49	47.47	50.59	49.52	47.56
245–270	10.57	10.91	12.67	11.78	12.75	13.18
270–320	16.09	14.84	14.66	14.62	14.68	15.88
Residue	13.30	13.70	13.00	13.75	13.08	12.19

From the results of these experiments it is apparent that the amount of creosote distilling between given temperatures is not very greatly influenced by rates of distillation varying from 1 to 3 drops per second. No determinations have been made to test the relative composition of these fractions, but a careful observation of them leads to the belief that there is a slightly better separation of the constituents when the distillation is run at about 1 to 2 drops per second.

TEMPERATURES FOR TAKING FRACTIONS.

It has already been pointed out that on account of the large number of constituents in creosote, the various substances do not volatilize at their boiling points. For this reason it is impossible to separate any of the constitutents of creosote in a state of purity by one distillation.

The naphthalene fraction contains many other substances besides naphthalene, and the amount of this compound in the so-called naphthalene fraction shows considerable variation. This is brought out in Table 3, on page 16.

It has been assumed that the greater part of the phenols present in creosote are obtained in the fraction between 200° and 210°. The volumes of phenols present in the various fractions obtained from several creosotes were determined with the results given below.

Table 6.—*Distribution of phenols in creosote fractions.*

[100 grams of oil used for each distillation.]

	170°.	170°–200°.	200°–210°.	210°–235°.	235°–270°.	270°–315°.
Creosote No. 3:						
Percentage distilling	0.0	0.0	0.0	11.95	33.96	27.99
Volume of phenols, c. c	0.0	0.0	0.0	2.2	4.9	2.8
Creosote No. 4:						
Percentage distilling	2.23	8.60	9.52	35.57	21.14	13.37
Volume of phenols, c. c	0.1	1.2	1.3	3.1	0.2	0.3
Creosote No. 5:						
Percentage distilling	3.69	3.70	6.73	32.04	22.13	17.84
Volume of phenols, c. c	0.3	0.0	0.6	2.6	0.2	0.4
Creosote No. 10:						
Percentage distilling	3.58	8.89	11.14	39.32	13.70	[illegible]
Volume of phenols, c. c	0.0	0.7	1.5	2.0	0.1	

From these results it is evident that a segregation of the phenols (using the word phenol as the general name for the aromatic hydroxy compounds) into the fraction between 200° and 210° is not accomplished. This is partly due to the fact that the phenols which, when pure, boil between these temperatures do not completely distill from creosote at their boiling points, and, further, to the presence of certain phenols, like the naphthols, whose boiling points are very much higher than 210°.

In attempting to decide upon the temperature ranges for taking fractions in making creosote analyses, the difficulties are increased by the fact that the varying composition of different samples of commercial creosote causes a shifting of the limits between which the constituents distill. As Doctor Alleman has pointed out, the naphthalene from a light oil will come off at a lower temperature than that from an oil containing a large amount of high boiling material.

In deciding upon the value of a creosote for any specific purpose in wood preservation, the greatest weight is attached to the quantities of light oil, naphthalene, and anthracene oil, respectively. In order to learn the temperature limits between which naphthalene and solid anthracene oil distill, a series of detailed fractionations have been carried out on six different creosotes and estimations made of the percentages of solids present in the different fractions. The distillations were made in 500 c. c. side-neck bulbs using 250 grams of oil. The results of this analytical work are presented in the form of curves (see figs. 8 to 14). Two curves are plotted together for each creosote analyzed. One is a cumulative curve showing the percentage by weight distilling as the temperature rises. The other curve shows the percentage of solids at 0° in the fractions between different temperatures. The percentage

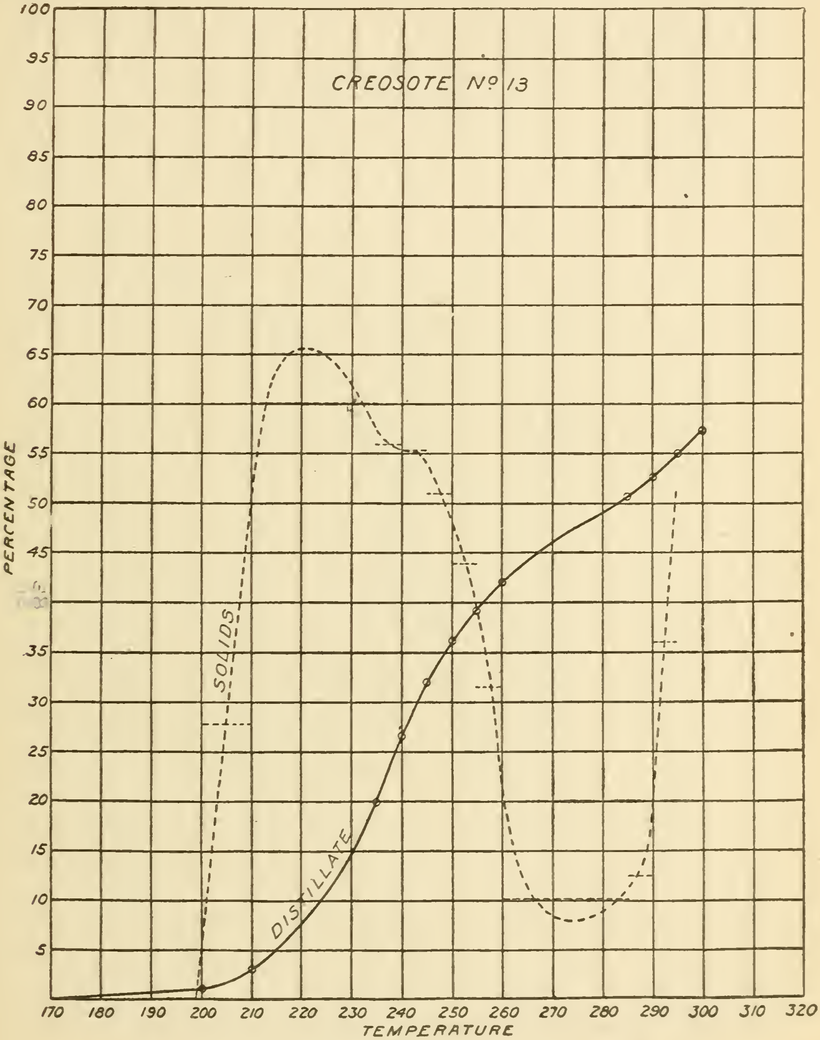

FIG. 8.—Distribution of solids in the distillate from creosote No. 13.

distillate curve is drawn as a solid line; the percentage of solids in the fractions is drawn as a dotted line.

It should be said that the curves showing percentage of solids are to some degree approximate; no *point* on such a curve can be located, since the amount of oil distilling at any point of temperature is insufficient for a naphthalene determination. Consequently the naphthalene must be estimated in the distillate from a range of temperature, and the determination represents the average composition through this range. The actual determinations are represented by horizontal dotted lines.

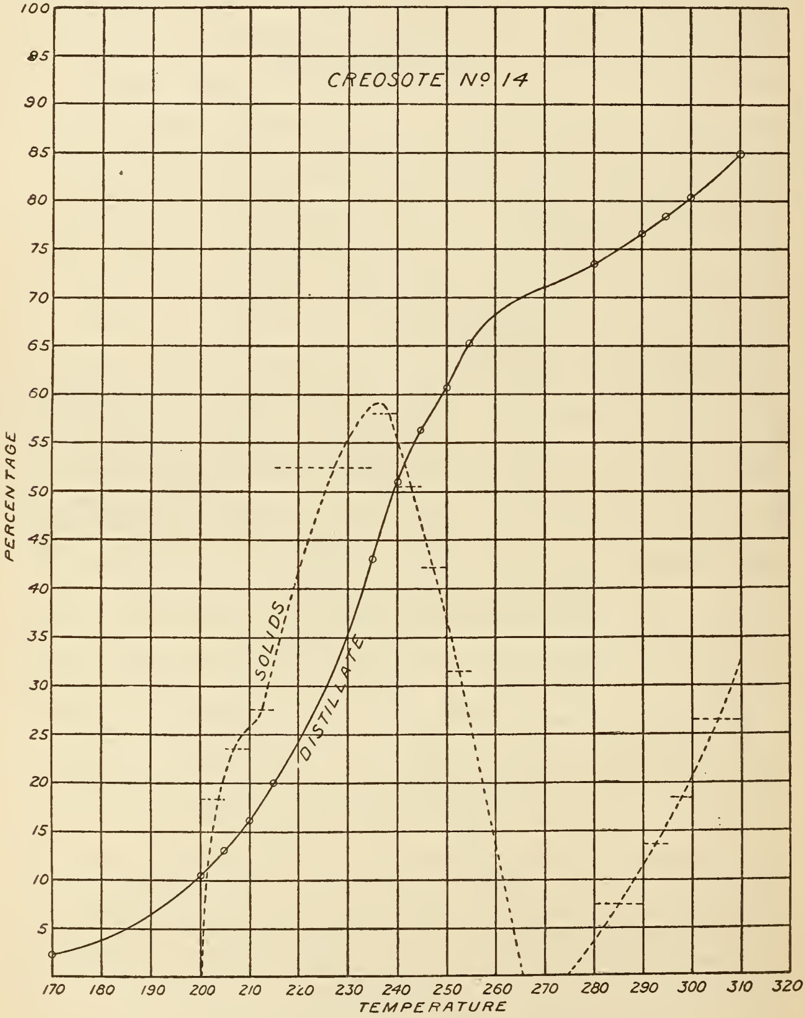

FIG. 9.—Distribution of solids in the distillate from creosote No. 14.

As may be seen from the curves, the six creosotes possess a wide range of properties. Number 13, for example, is a high boiling creosote containing a large quantity of anthracene oil, as brought out in analyses given earlier in this paper, although the present distillation

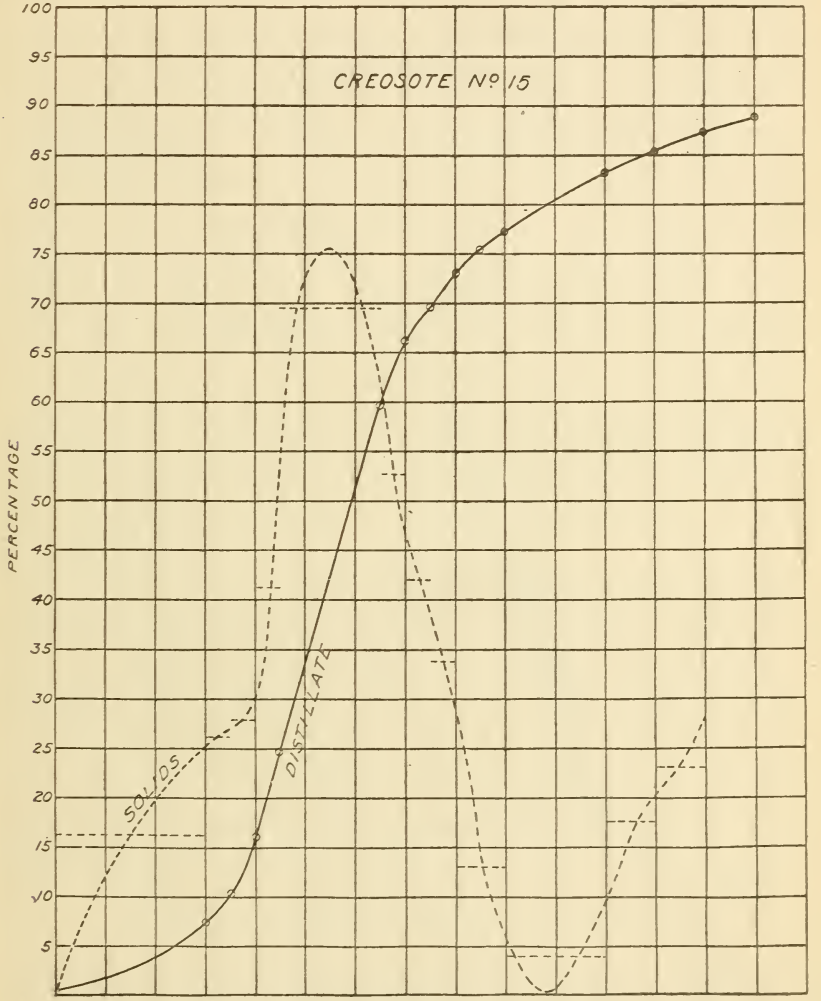

FIG. 10.—Distribution of solids in the distillate from creosote No. 15.

was not carried beyond 300°. In contrast to this, No. 39 is a very light oil with a relatively low content of naphthalene in the naphthalene fraction. As might be expected, the curves of these different creosotes show marked variations.

The average curve of the six creosotes is shown on page 28. The question of the temperatures for taking the fractions depends upon how low a concentration of naphthalene should be included in the naphthalene fraction, and how low a content of solids in the anthracene fraction. If one were to decide on 25 per cent of solids as the critical amount, the temperatures for fractions would be in round numbers:

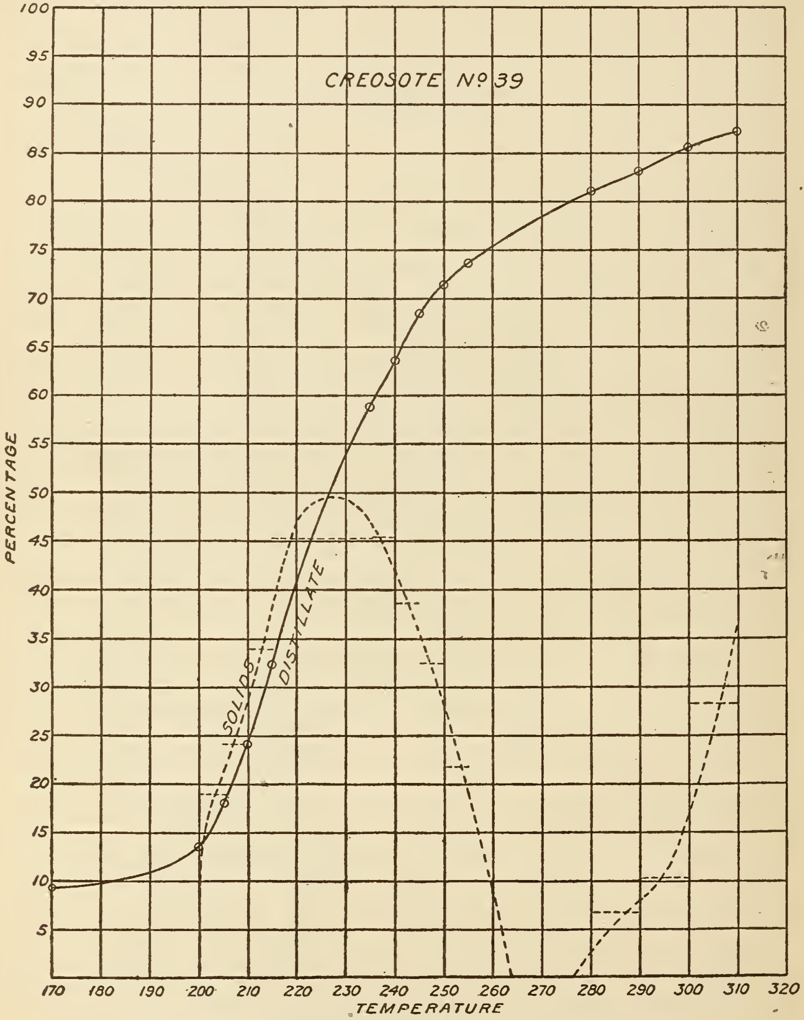

Fig. 11.—Distribution of solids in the distillate from creosote No. 39.

Fraction No. 1: To 205° = light oil fraction.
Fraction No. 2: 205° to 250° = naphthalene fraction.
Fraction No. 3: 250° to 300° = heavy liquid fraction.
Fraction No. 4: 300° to end = anthracene oil fraction.

It is a common experience to have the fraction between 245° and 270° C. remain liquid at room temperature. In the detailed fractionations it was found that in several instances the fractions between 255 and 280 was liquid even at 0°. Two of these liquid fractions were redistilled from small bulbs, with the results given in Table 7.

TABLE 7.—*Redistillation of fraction 255°–280°.*

Creosote No. 14 (18.38 grams).			Creosote No. 41 (15.04 grams).		
Temperature (first drop at 218°).	Weight of fractions.	Character.	Temperature (first drop at 210°).	Weight of fractions.	Character.
Degrees.	*Grams.*		*Degrees.*	*Grams.*	
218–250	6.85	Many naphthalene crystals.	210–250	5.10	Liquid at 23°; some naphthalene at 0°.
250–260	3.41	Liquid.	250–255	1.57	Liquid.
260–265	1.71	Do.	255–260	1.28	Do.
265–270	.37	Do.	260–265	1.19	Do.
270–275	.66	Do.	265–275	1.56	Do.
275–285	1.71	Liquid, with a few yellow crystals.	275–280	1.34	Do.
Residue	3.30	Thick, with fine crystals.	Residue	2.56	Thick, with fine crystals.

The fact that the first fractional distillation fails to effect an efficient separation is brought out in a striking way in figure 15 (page 29), where the results of the fractional distillation of the liquid fraction of No. 14 are plotted as a curve on the same sheet with the curve showing the original fractionation of the creosote.

It was thought that two of the physical properties of creosote fractions, the index of refraction and the specific gravity, might be of service in determining the temperature for taking fractions. The index of refraction was measured at 60° C.; the specific gravity was determined by comparing the weight of a volume of the oil at 60° C. with the weight of an equal volume of water at that temperature. The results obtained by making these determinations on the 14 or 15 fractions obtained by a detailed fractioning of three creosotes have been plotted as curves and are shown in figures 16 and 17, on pages 30 and 31. This line of investigation is not yet concluded.

SOURCES OF ERROR IN CREOSOTE FRACTIONATION.

There are three sources of error which are likely to cause material differences in analyses made by different workers.

(1) The accuracy of thermometers, even high-priced ones, is problematical. One of the thermometers used in the experiments reported, the list price of which was $10, showed errors ranging from 1.4° at 200° to 6° at 500°. A cheaper, nitrogen-filled thermometer showed a rise in the zero point of 23° after being heated to a high temperature.

When using thermometers for high-temperature work it is necessary, therefore, that great care be exercised to insure their accuracy.

(2) The readings of the thermometer are too low on account of the emergent thermometer stem being at a lower temperature than the portion in the vapor. On the thermometers which were used in the experiments detailed above this correction amounts to about 2.3° at 240°, and about 8° at 360° C. No corrections for the emergent thermometer stem have been made, since such corrections are not ordi-

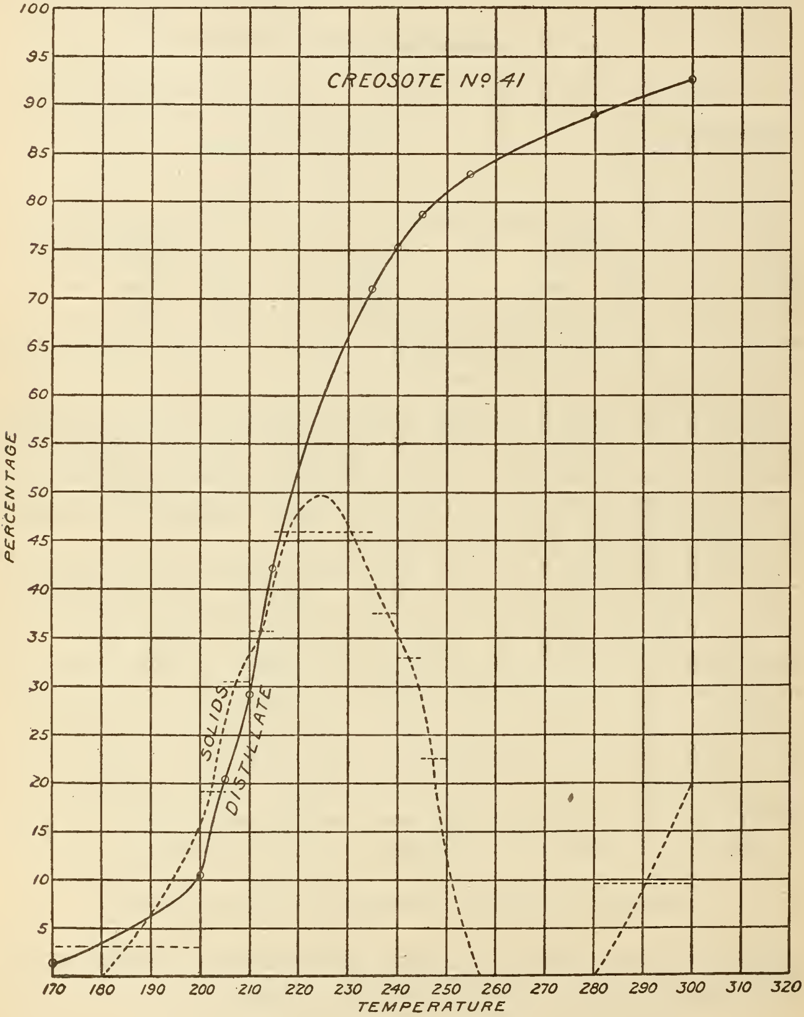

FIG. 12.—Distribution of solids in the distillate from creosote No. 41.

narily made in creosote analyses. It is probable that the amount of this correction would be nearly the same for the thermometers used by different analysts, so that no great variation in results should come from this source.

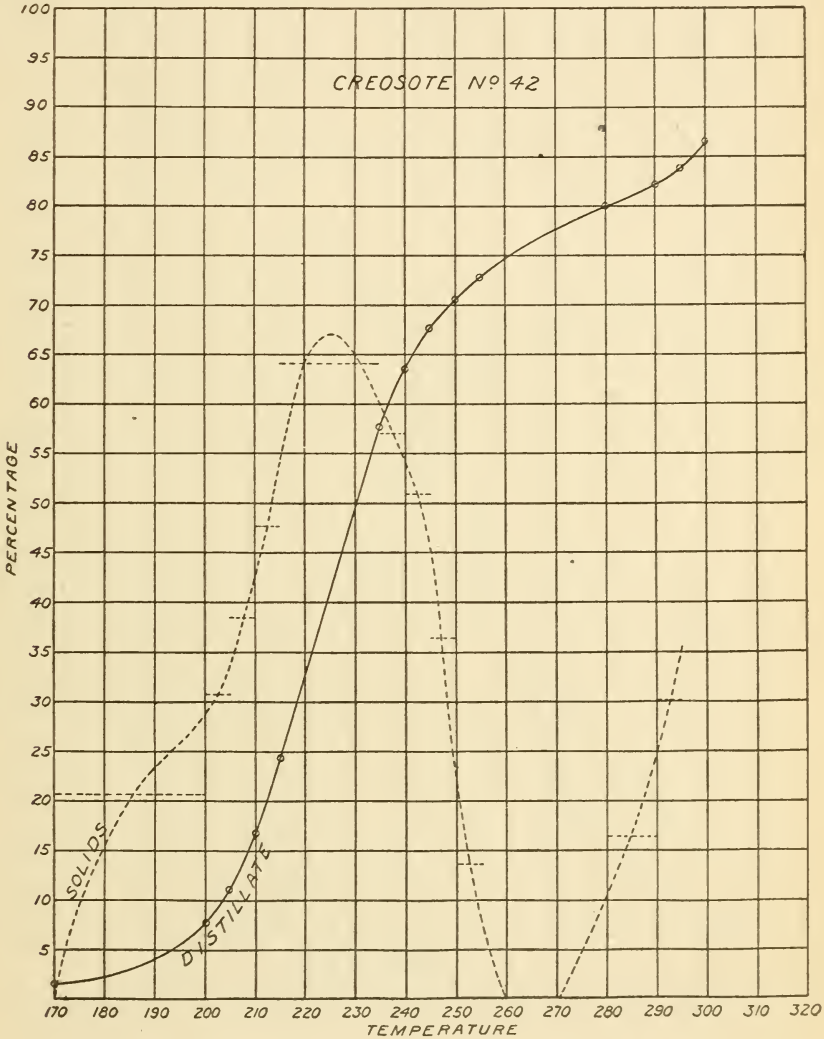

FIG. 13.—Distribution of solids in the distillate from creosote No. 42.

(3) It is very essential that a creosote sample be absolutely liquid before the quantity used for distillation is weighed out, since a small amount of unliquefied naphthalene will produce an appreciable error in the results of the distillation. It is not at all improbable that the

samples sent to the laboratory for analysis may not represent the average composition of the creosote under examination, and this may or may not be under the control of the analyst, but it is possible for him to obtain a perfectly representative sample of the oil which is brought into the laboratory.

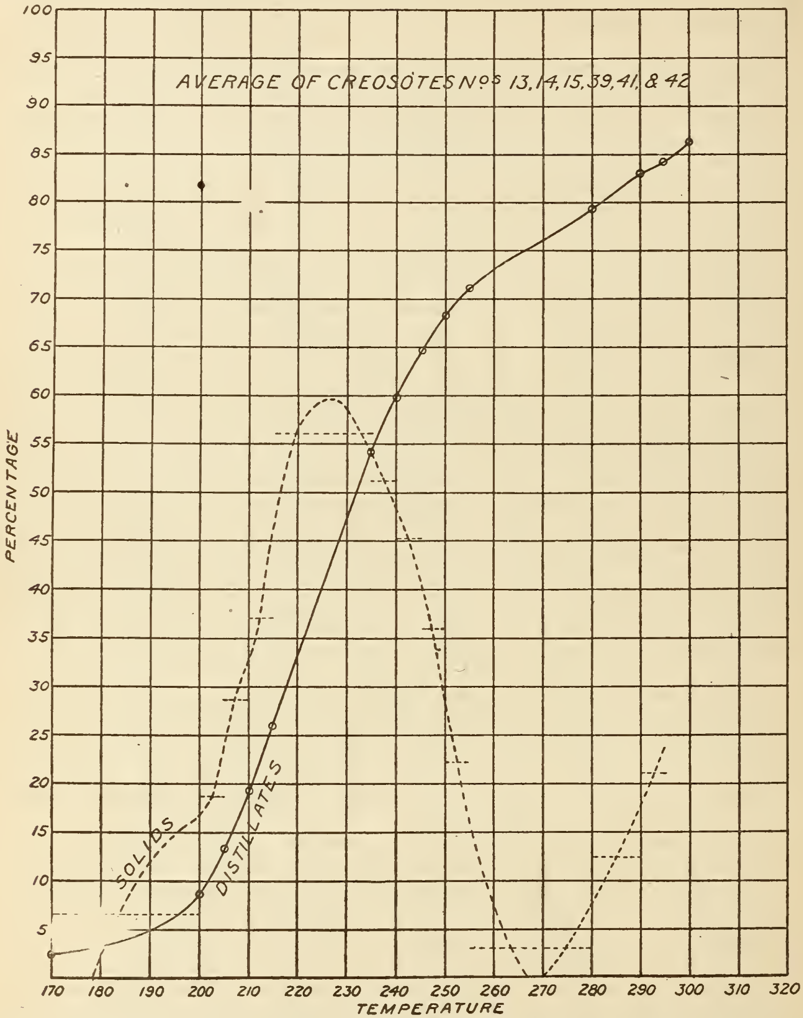

FIG. 14.—Average distribution of solids in the distillates from creosotes Nos. 13, 14, 15, 39, 41, and 42.

SUMMARY.

(1) Provided all other conditions are kept constant, the weights of the various fractions distilled from creosote do not differ to a marked degree when using a retort, an ordinary distilling flask, or a three-bulb Ladenburg flask.

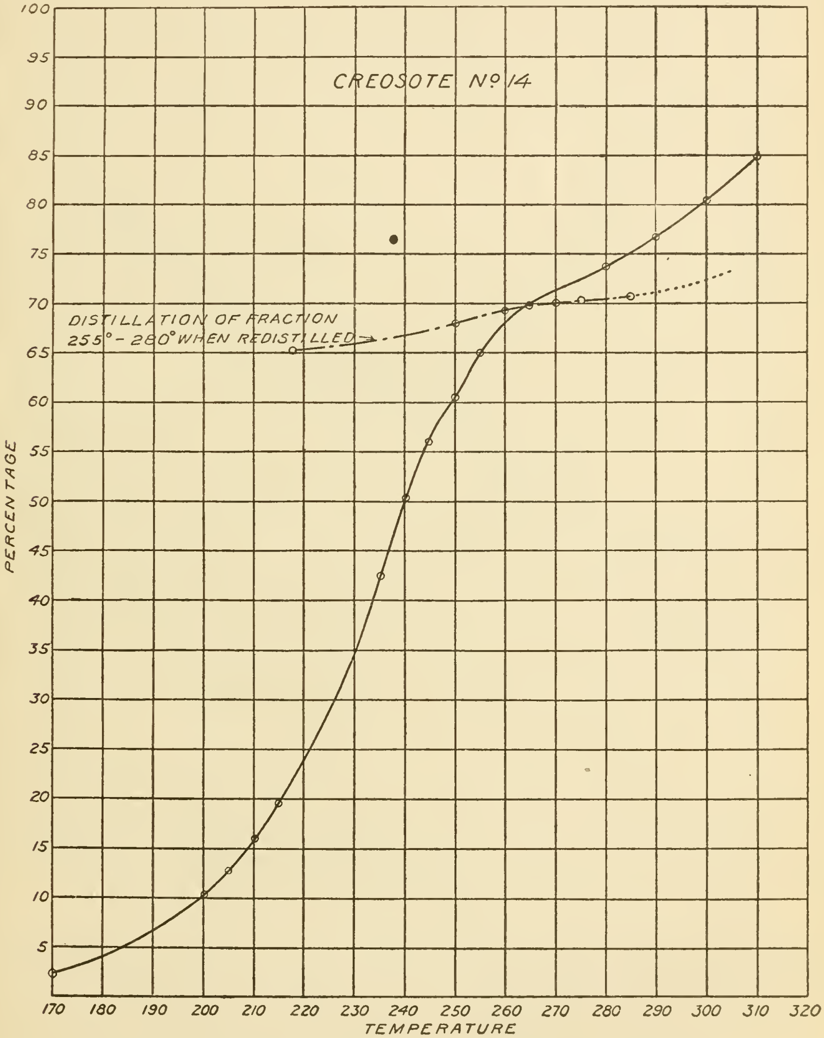

FIG. 15.—Redistillation of the fraction from 255°-280° of creosote No. 14.

(2) In so far as the amount of solids (naphthalene and solid anthracene oil) is a criterion, the fractionation is slightly sharper when using a flask than when using a retort.

(3) If the relation between the size of the distilling vessel and the amount of creosote distilled is approximately constant, the size of the distilling vessel has no influence on the percentage weights of the fractions.

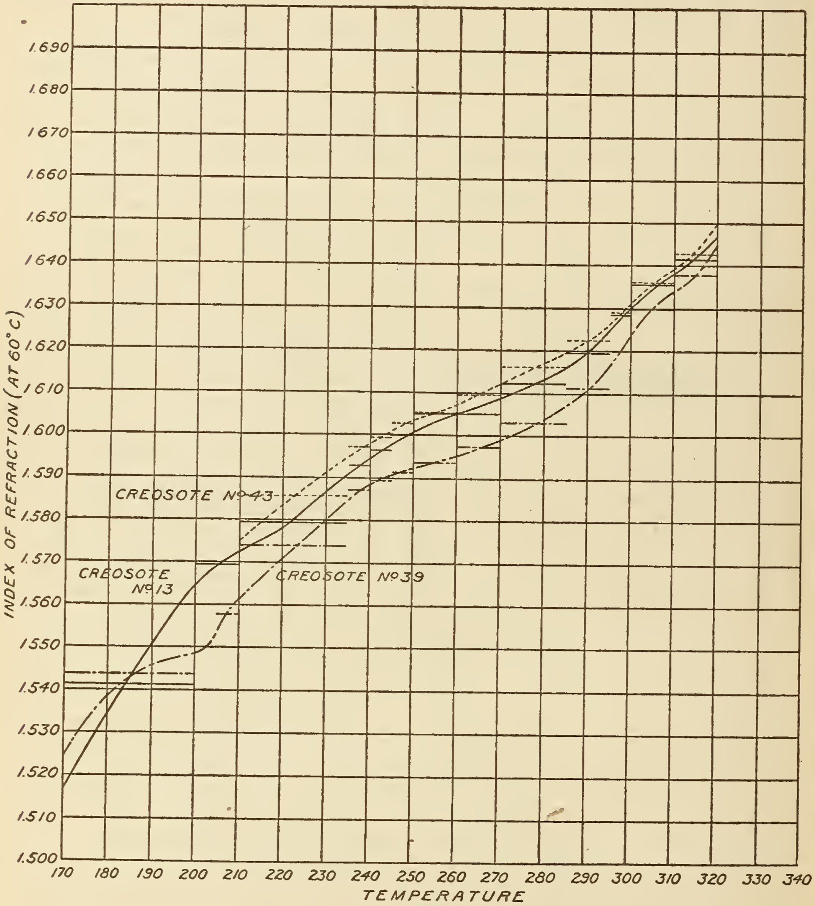

Fig. 16.—Refractive indices of the fractions from creosotes Nos. 13, 39, and 43.

(4) The rate at which a creosote distillation is carried out has some influence on the weight of the fractions obtained, although the differences obtained by varying the rate of distillation are not large.

(5) The temperatures between which naphthalene and the anthracene oil solids distill were determined for six creosotes. The individual

results and the average of the six are plotted. The results show marked variations between the different creosotes, and the average furnishes one criterion for determining the temperatures between which fractions should be taken.

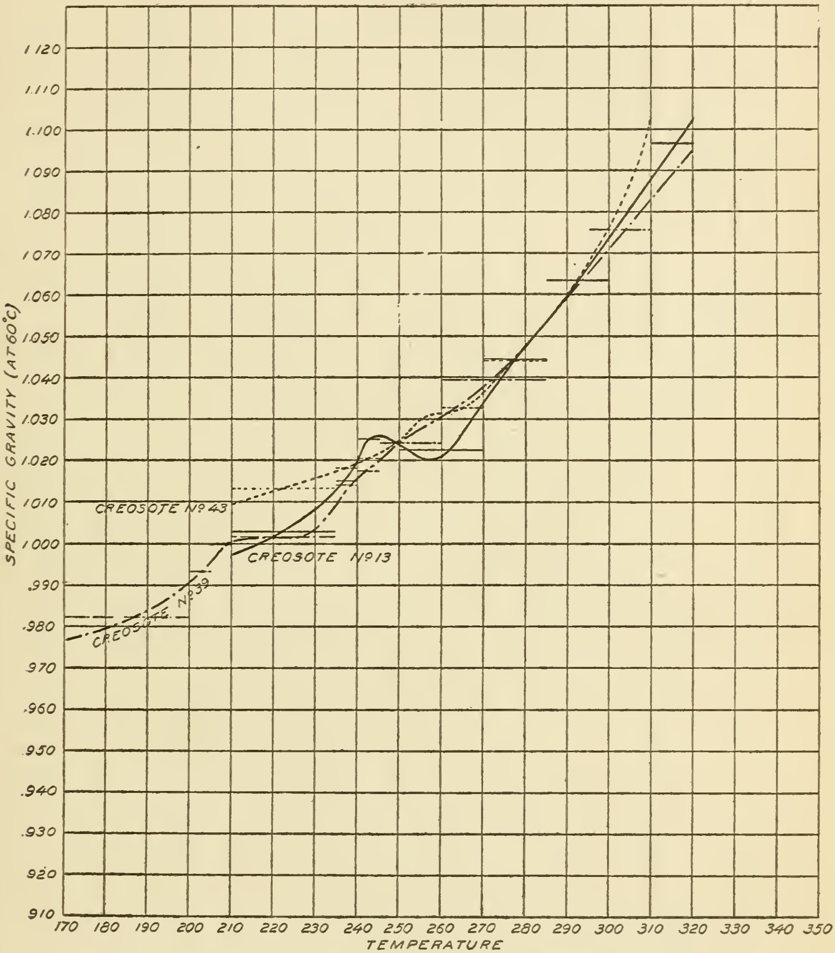

FIG. 17.—Specific gravities of the fractions from creosotes Nos. 13, 39, and 43.

(6) The specific gravity and index of refraction of a large number of fractions of three creosotes were determined. This line of study is not yet complete.

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